

Regioselectivity in Cycloaddition Reaction Between Phosphaacetylene and Diazomethane: An *Ab Initio* Study

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ABSTRACT

The [3 + 2] cycloaddition reaction of phosphaacetylene with diazomethane was investigated by means of high level *ab initio* calculations. It was deduced that the aromatic diazaphosphole is formed via a nonaromatic intermediate. The regiospecificity of the reaction is thus determined by the energy difference between the two transition states that lead to the two possible regioisomeric intermediates. Of the transition states in the concerted pathways, the one leading to the regioisomer with two PC bonds (3) was found to be more stable at all the levels of theory investigated, including coupled-cluster singles doubles (CCSD(T)/6-311 + G*/Møller-Plessett(MP)2/6-311 + G* (+basis set superposition, BSSE, correction). The energy difference between the two transition states, however, is always less than 2 kcal/mol. When the free energies in the two reactions are calculated by use of the harmonic frequencies, the energy separation between the two transition structures remains practically unchanged. The free energy of activation ΔG^\ddagger was 21 kcal/mol at the CCSD(T)/6-311 + G* level of theory and use of the MP2/6-31 + G* frequencies. At the MP2 level, a rather stable complex is obtained in the initial phase of the reaction. However, the stability of the complexes decreases at the CCSD(T) level, and application of the BSSE correction results in unstable complexes. © 1997 by John Wiley & Sons, Inc.

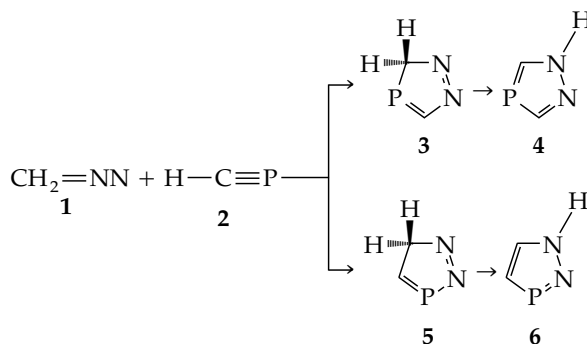
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Introduction

Cycloaddition reactions¹ play an important role in organic chemistry and have thus attracted considerable theoretical interest. While semiquantitative theories such as frontier molecular orbital theory (FMO)² or perturbational molecular orbital theory (PMO)³ were found to be extremely successful in predicting the regiochemistry of products in reactions of these types,⁴ there are also cases that cannot be treated by such simple considerations. One example for this is the subject of the present article.

Phosphaalkynes easily undergo cycloaddition reactions of the [2 + 2], [3 + 2], and [4 + 2] type by which a vast number of heterocyclic unsaturated phosphorus compounds are accessible.⁵ In the case of the experimentally well-investigated reaction of diazo compounds with phosphalkynes, a high regioselectivity is almost never found.⁶ Even for the parent system investigated here of diazomethane (1) and phosphacetylene (2) the reaction runs regiospecific⁷ and proceeds even at rather low temperatures. The latter observation indicates that the activation barrier of the reaction is quite small. In fact only the reaction of phosphacetylene with *t*-butyl diazoacetate is known to afford both regioisomers.⁷ While the rather low lying lowest unoccupied molecular orbital (LUMO) of phosphacetylene⁸ gives rise to a low energy transition state, the nearly equal molecular orbital (MO) coefficients (of phosphorus and carbon) in both highest unoccupied molecular orbital (HOMO) and LUMO are not in harmony with the regiospecific product distribution. Furthermore, it is known that when a C—C bond in a reactant is replaced by P—C unit, the resultant products are analogous and even the rate constants of the reactions remain similar,⁹ a finding that can be extended to alkynes and phosphalkynes as well.

The mechanism of the reaction of 1 with 2 under investigation here was postulated elsewhere.⁵⁻⁷ In the first step, a nonaromatic 3*H*-1,2,4-diaaphosphole (3) is formed that then undergoes rearrangement to the aromatic 1*H*-1,2,4-diazaphosphole (4) by way of a [1,5] sigmatropic proton shift (see Scheme 1). In the cases of some substituted reactants, it has even been possible to isolate the corresponding 3*H*-1,2,4-diazaphosphole (3) derivative,⁶ thus substantiating the putative mechanism under consideration. In contrast, the other feasible products (5 and 6) have, with one



SCHEME 1

exception, never been detected, which proves the regioselectivity of the reaction.

The apparent contradiction between the expected low regioselectivity and the experimental results prompted us to investigate the reaction of diazomethane with phosphacetylene by means of *ab initio* quantum chemical calculations. The early quantum chemical calculations on dipolar cycloadditions were summarized by Houk and Yamaguchi.¹⁰ Basically, two possible mechanisms exist for dipolar cycloaddition reactions: the concerted and the biradical path. Although it has been advocated by correlated *ab initio* calculations that the biradical path is favored,¹¹ more recent studies, with the help of the Mulh configuration self-consistent field (MCSCF) technique¹² (which allows a treatment of both closed and open shell systems on an equal footing), led to the conclusion that the energetically favored transition state is the concerted and not the stepwise biradical one. Similar results have also been reported for the thioformaldehyde + diazomethane reaction.¹³ In some [2 + 2] cycloaddition reactions, however, it was shown that the concerted and the nonconcerted pathways are quite similar in energy terms.¹⁴

The aim of the present work was to investigate the concerted pathway of the cycloaddition reaction between HCP and CH₂—NN by quantum chemical methods at different levels of theory in order to rationalize the high regioselectivity of the reaction.

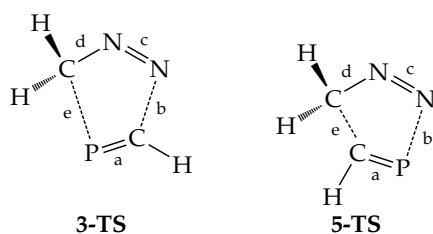
Calculations

Quantum chemical calculations were carried out by the Gaussian 92 suite of programs.¹⁵ Geometry optimizations were carried out for all the compounds treated here at the Hartree-Fock (HF)/6-31G* and at the Møller-Plesset (MP)2/6-31G* levels of theory. For the stationary

points obtained, second derivative calculations were performed to show that the structures are real minima or first-order saddle points on the respective potential energy surfaces.

In the cases of the two most important saddle points (**3-TS** and **5-TS**, transition state, see Scheme 2), further calculations were carried out. To investigate the effect of any possible biradicaloid electronic structure in the transition states, the optimizations were repeated by the unrestricted HF (UHF) method as well; however, the UHF wave function always collapsed to the restricted HF (RHF) function. The stationary points were reoptimized at the CASSCF(6,5)/6-31G* level as well. The choice of the active orbitals was in accordance with earlier calculations^{12,13} for other dipolar cycloaddition reactions, where it had been shown that the role of the out of plane ($\pi -$) orbitals was minor during the course of the reaction and that mainly the "former" π orbitals of the reactants (now in plane) were involved.¹¹ The reference configuration had a configuration interaction (CI) coefficient of 0.95; most of the other important configurations (one having a value of about 0.2, two others having somewhat larger than 0.1) resulted from double excitations for both transition structures. The minima and transition structures were further reoptimized using the density functional theory (DFT), as implemented in the Gaussian 92/DFT package,¹⁶ using Becke's correlated functional.¹⁷ The adequacy of DFT calculations on some dipolar cycloaddition reactions was recently demonstrated.¹⁸ Further optimizations were carried out at the MP2/6-31 + G* and MP2/6-311 + G* levels of theory for some of the most important, loosely bound structures. Second derivatives were calculated, however, only at the MP2/6-31 + G* level for reasons of economy, because the structural changes were only minor when using the larger basis set.

To account for basis set superposition error (BSSE), a counterpoise correction¹⁹ was considered for the loosely bound structures and transition structures.



SCHEME 2

Single point CCSD(T)/6-311 + G*//MP2/6-311 + G* calculations were also carried out to study the effect of the different levels of electron correlation on the relative energies of the transition state and to test the reliability of the results obtained. The single point second-order multiconfigurational perturbation theory (CASPT2) was used as well to account for the dynamic and nondynamic parts of the correlation energy by the MOL-CAS-3 package.²⁰

Results and Discussion

EQUILIBRIUM STRUCTURES

The relative energies of the starting materials (**1** and **2**), putative intermediates (**3** and **5**), and products (**4** and **6**) of the investigated reactions are compiled in Figure 1 at the MP2/6-31G* level of theory (HF/6-31G* data are given in parentheses). From the data, it is apparent that inclusion of an electron correlation results only in minor changes in the relative energies of the stable compounds. According to the density functional calculations, the relative stabilities for **3** and **5** are somewhat smaller with respect to the reactants (−33 kcal/mol). These changes, however, do not have a significant impact on the exothermic nature of the reaction. The relative stabilities of the products (**4** and **6**) and intermediates (**3** and **5**) with respect to the starting materials support the original proposal about the two step mechanism (initial cycloaddition and subsequent isomerization to the stable aromatic²¹ form). Because each of the intermediates (**3** and **5**) is at a much lower energy (by ca. 40 kcal/mol) than the starting materials, the possibility of any back reaction is very low. The energy difference between **3** and **5** is much smaller than the exothermicity of the reaction; therefore thermodynamic control should not be operational in the present case. From the calculated harmonic frequencies of the intermediates (**3** and **5**), those having the lowest energy correspond to the asymmetric, out of plane movement of the two hydrogens on the same carbon atom, leading obviously to the transition state of the [1,5] sigmatropic H shift. Because these harmonic frequencies are 288 and 343 cm^{−1} (for **3** and **5**, respectively), the corresponding barriers should be not too large, and were not considered further.

All the above findings support the previous hypothesis that the course of the whole reaction

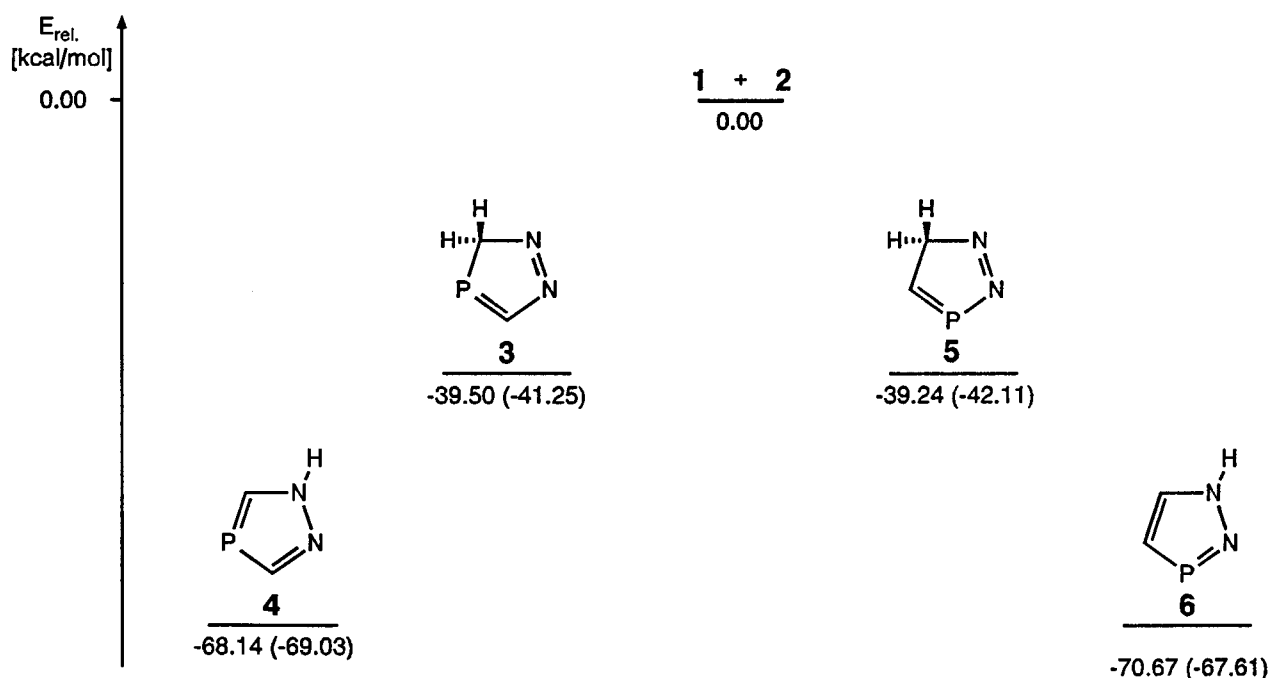


FIGURE 1. Relative Energies of Educts, Intermediates, and Products at MP2/6-31G* Level of Theory (HF/6-31G* values given in parentheses).

will be determined by the transition state of the cycloaddition reaction; and it seems likely that the regioselectivity problem would be resolvable if the relative energies of the transition states of this part of the reaction were known.

TRANSITION STRUCTURES

The transition structures (3-TS and 5-TS, Scheme 2) leading to both regioisomers were first optimized at the HF/6-31G* level of theory. The energy difference between the two transition struc-

tures in favor of 3-TS by 0.87 kcal/mol, with barriers of about 20 kcal/mol with respect to the reactants. This barrier is similar to those calculated previously for other dipolar cycloadditions,¹ although on the basis of the low lying LUMO of HCP a somewhat lower barrier would be expected.

When the optimizations were repeated at the CASSCF(6,5)/6-31G* level, the resulting transition structures did not differ significantly from those obtained at the HF/6-31G* level (Table I). For both transition structures, the reactants exhibit

TABLE I. Important Structural Parameters for Transition States 3-TS and 5-TS.

Level of Theory	3-TS						5-TS					
	a	b	c	d	e	CNN	a	b	c	d	e	CNN
HF ^a	1.553	2.306	1.115	1.364	2.348	145.7	1.560	2.775	1.113	1.340	2.134	151.1
CAS ^a	1.563	2.348	1.133	1.363	2.349	143.6	1.565	2.749	1.132	1.348	2.204	147.1
MP2 ^a	1.581	2.419	1.169	1.342	2.622	153.2	1.590	2.715	1.168	1.341	2.352	154.5
MP2 ^b	1.583	2.439	1.169	1.347	2.632	153.3	1.592	2.715	1.166	1.344	2.371	154.7
MP2 ^c	1.580	2.441	1.160	1.340	2.620	153.3	1.588	2.729	1.158	1.343	2.364	154.7
BLYP ¹	1.584	2.501	1.166	1.349	2.586	150.6	1.589	2.848	1.164	1.336	2.372	154.6
BLYP ^c	1.583	2.490	1.159	1.355	2.536	149.1	1.588	2.832	1.157	1.339	2.337	153.3

Bond length are in angstroms and bond angles in degrees.

^{a-c} 6-31G*, 6-31 + G*, and 6-311 + G* basis sets, respectively. For the notations used see Scheme 2.

a somewhat larger separation than in the HF case, indicating that the CASSCF procedure predicts a slightly earlier transition state than the HF method. Structure **3-TS** was again found to be lower in energy than **5-TS** at this level of theory (by 0.64 kcal/mol). The CASSCF wave function is dominated by the HF reference (see Calculations section).

The MP2 transition structures differ significantly from those obtained at the HF and MCSCF levels of theory. A reaction coordinate can be defined where the average changes of the bond lengths (bonds a, c, and d in Scheme 2) are set to 0% for the reactants and 100% for the products, respectively.²² While the HF and CASSCF transition structures are placed at 35 and 30% along this reaction coordinate, respectively, the MP2 transition structure shows a value of 15%, indicating a somewhat earlier transition state. Because CASSCF is able to pick up some part of the dynamic electron correlation, it is reasonable that this structure lies between those obtained at the HF and MP2 levels; furthermore, it indicates that the perturbed HF wave function gives a reasonably good description, at least in the early reaction coordinate region.

The energies of the transition structures (with respect to the reactants) are significantly smaller at the MP2 than at the HF level of theory. The **3-TS** structure is again somewhat lower in energy (by 1.68 kcal/mol) than **5-TS**. (It has been noted before that the energy difference of the transition states leading to regioisomers is usually well predicted at low levels of theory, while the activation barrier itself is subject to significant changes as the level of theory is changed.)^{23,24} In fact, the energy of

3-TS is *negative* with respect to the starting materials; therefore, an additional minimum at large internuclear separations should be present on the MP2/6-31G* potential surface, while **5-TS** is only 0.08 kcal/mol above the energy of the starting materials. This rather low activation barrier, because it is based on the single determinant wave function, is likely to be even lower when other references are included.

Because the MP2 transition state is at an early phase of the reaction and a complex at an even higher internuclear separation should be dealt with as well, the inclusion of diffuse functions in the basis set is necessary. Accordingly, further calculations were carried out using the 6-31 + G* and 6-311 + G* basis sets.

The geometries and relative energies of **3-TS** and **5-TS** change only slightly upon the MP2 reoptimization. Although both structures are further stabilized with respect to the starting material, the stabilization is more pronounced in the larger basis set. DFT/6-311 + G* calculations resulted in similar structures for **3-TS** and **5-TS** as obtained at the MP2 level, thus further supporting the early transition state for the reaction. Similar conclusions can be drawn by comparing the dipole moments of the transition states as well. The calculated dipole moment of **3-TS** and **5-TS** are 1.70–1.86 and 2.31–2.57 D, respectively, at the MP2 optimized geometries (early transition state). At the HF and CASSCF levels (transition structure is later on the reaction coordinate, see above), the dipole moment of **3-TS** changes only slightly (1.60–1.79 D), while in case of **5-TS** a considerable change (to 3.01–3.20 D) is observed. (The calculated dipole moment of **3** is 2.23 D, while –0.78 D is calculated for **5**; thus,

TABLE II.
Relative Energies of Transition States and Loosely Bound Complexes with Respect to Starting Materials, Including MP2/6-31 + G* ZPE-s.

	MP2 / 1 ^a	MP2 / 1 / 2 ^b	CCSD(T) / 1 / 2 ^c	DFT / 2 ^d	ΔG
3-TS	–0.28	–1.34 / + 3.10	+5.70 / + 10.34	7.98	21.06
5-TS	+1.33	+0.62 / + 2.31	+7.50 / + 11.24	8.91	21.91
3-CO	–2.84	–3.52 / – 1.22	–0.84 / + 1.57	—	
5-CO	–2.43	–2.91 / – 1.01	–0.76 / + 1.25	—	
– E_{tot} reactants	527.65821	527.74742	527.81179	528.75996 ^e	

Values separated by / refer to the uncorrected and BSSE corrected results, respectively.

^a Using the 6-31 + G* basis.

^b Using the 6-311 + G* basis.

^c Using the 6-311 + G* basis at the MP2/6-311 + G* geometry.

^d Total energy of **3-TS**.

^e Free energy changes were calculated using the CCSD(T) / 6-311 + G* // MP2/6-311 + G* energies, and the MP2/6-31 + G* frequencies. Internal rotations were considered (see text).

in the reaction path leading to **3**, the change in the dipole moment is much smaller than in the competing reaction pathway.) If the transition state were not at an early phase of the reaction, the use of a polar solvent should stabilize **5-TS** with respect to **3-TS**, thus changing the product ratio. However, such a behavior has never been reported and so the early transition structure is in accordance with the experimental results in this respect.

In view of the small energy differences between **3-TS** and **5-TS** and the significant changes in the reaction barriers between the different correlated levels, a further refinement of the calculations was necessary. To better account for the influence of electron correlation effects CCSD(T)/6-311 + G*//MP2/6-311 + G*, as well as CASPT2/6-31G*//CAS(6,5)/6-31G*, calculations were carried out and the effect of BSSE was considered by a counterpoise correction.^{19,25} By using the MP2/6-31 + G* harmonic frequencies, ΔG^\ddagger values were calculated and are summarized in Table II.

On the basis of the results collected in Table II, the most immediate conclusion is that **3-TS** is more stable than **5-TS** at every level of theory, including the density functional method. The use of the larger basis set increases the relative stability of **3-TS** somewhat to nearly 2 kcal/mol; however, the effect of BSSE is to reduce the separation by about 1 kcal/mol, reflecting the fact that **5-TS** is located somewhat earlier on the reaction coordinate according to the atomic distances (Table I). CASPT2/6-31G* energy calculations on the CAS(6,5)/6-31G* optimized geometries resulted again in an energy difference of 1.45 kcal/mol between **3-TS** and **5-TS**, similar to the MP2/6-31G* case, indicating the adequacy of the single determinant based wave functions. The method used to account for the electron correlation has little effect on the relative energies of **3-TS** and **5-TS**.

As for the barrier to the reaction itself, MP2 results seem to be too low; all other correlated methods as well as DFT calculations give barriers that are higher by 5–7 kcal/mol. The BSSE correction (near 3–4 kcal/mol) acts to increase the energy of the transition structures further with respect to the reactants.

The calculated molar volume of **3-TS** is about 5% less than that of **5-TS**, thus stabilizing the reaction via **3-TS** by the $p\Delta(\Delta V^\ddagger)$ product. However, at atmospheric pressure this results in an energy difference of merely a few hundredths of 1 kcal/mol.

Because the reaction (carried out at constant pressure and temperature) is governed by the free energy rather than by the energy of the transition state, the ΔG^\ddagger values of the two reactions should be considered as well. One of the harmonic frequencies corresponded to an internal rotation motion for both **3-TS** and **5-TS**; therefore, the contribution of these frequencies to the thermal energy and entropy were replaced by values corresponding to the internal rotation. The inclusion of the entropy factor has a rather large impact on the activation barrier; this behavior, however, is characteristic for association reactions. Although the changes in the free energy of the two transition structures are large upon inclusion of the entropy factor, the energy difference between **3-TS** and **5-TS** is not susceptible to these dramatic effects. It is worthy of note that the observed reaction conditions (5–10 min reaction time at –30 to 0°C) are in accord with a reaction barrier of about 10–15 kcal/mol.

According to the Curtin–Hammond principle, the product distribution is determined by the difference of the free energies of the two transition states. The 0.85 kcal/mol difference in ΔG^\ddagger , obtained at the highest level of theory [CCSD(T)/6-311 + G*//MP2/6-311 + G* + BSSE] would result in a 1:10 ratio of the product concentrations, when the BSSE was not considered by the counterpoise method, the difference of the free enthalpies of the transition structures was 2.5 kcal/mol, resulting in a product ratio of 1:150. Although the counterpoise method overcorrects, as has been discussed in the literature, according to the most recent view²⁵ it is still the best way to estimate the effect of BSSE.

COMPLEXES

Because MP2/6-31 + G* and MP2/6-311 + G* transition structures are lower in energy by a few kilocalories/mole than the reactants, it might be possible that the course of the reaction is determined by a loosely bound complex. Thus, structures of these types also require investigation. HF/6-31 + G* optimization of the loosely bound complexes (**3-CO** and **5-CO**) was attempted without success. At the MP2/6-31 + G* level, however, stationary points were found, as shown by the positive harmonic frequencies obtained from (MP2/6-31 + G*) second derivatives. Both structures show only slight distortion of the reactants, the changes in the bond lengths, for example, being less than 0.005 Å, while the NNC angle in

the diazomethane fragment is 172–174° (see Table III; for diazomethane the CNN angle is 180° at the MP2 level²⁶). The reactants in both complexes are found at an internuclear separation of about 3.3 Å. The **3-CO** complex is found to be somewhat lower in energy than the **5-CO** complex (Table II). At the DFT/6-31 + G* level, however, no stable complexes were obtained. The geometry optimization resulted in a structure in which the reactants are separated by 6–7 Å. The density functional method, on the other hand, is known to give spurious results for loosely bound complexes.²⁷

CCSD(T)/6-311 + G*//MP2/6-311 + G* calculations indicate that the stability of the complexes is overestimated at the MP2 level. When the effects of BSSE are considered, the complexes become unstable (see Table II). It should be noted on the other hand that, in the ozone + ethylene [3 + 2] cycloaddition reaction, early van der Waals complexes were reported²⁸ on the basis of microwave spectroscopic results as well as from *ab initio* calculations. For other [3 + 2] cycloadditions, Sustmann et al, also found stable complexes.²⁹

From the second derivative calculations of the two complexes (**3-CO** and **5-CO**), it becomes apparent that the lowest frequency corresponds to the internal rotation of the two reacting fragments (60 and 76 cm⁻¹ for **5-CO** and **3-CO**, respectively). Therefore, we optimized the transition state corresponding to this internal rotation at the MP2/6-31 + G* level, the result being a barrier of 1.58 kcal/mol. This activation energy lies below the barrier to the cycloaddition reaction. Neither the possible formation of the complexes nor their mutual transformation to each other should affect the course of the reaction significantly.

Conclusions

From investigations on the cycloaddition reaction between diazomethane (**2**) and phosphacetylene

(**1**) by *ab initio* methods, full support was obtained for the original assumption^{5–7} that the reaction produces first an intermediate (**3** or **5**, respectively) that subsequently rearranges to the product (**4** or **6**, respectively). The difference of the barriers leading to **3** or **5** should be responsible for the observed regioselectivity of the reaction, which is under kinetic control.

From the investigation of the two possible concerted pathways carried out at different levels of theory, including CCSD(T)/6-311 + G*//MP2/6-311 + G*, it was found that the transition state leading to **3** is always at a lower energy than the one leading to **5**. The energy difference, however, is only about 1–2 kcal/mol, depending on the level of theory used. Inclusion of the effect of BSSE by a counterpoise correction results in some decrease of the energy separation between the two transition states. When considering the entropy factor to obtain ΔG^\ddagger , the change in the relative free energies of activation is again very small. The effect of the differences on the molar volumes of the transition states is also found to be minor.

The free energy of activation of the reaction at the highest level of theory is about 21 kcal/mol, a value indicating that the reaction can proceed at room temperature at a reasonable rate. From the published reaction conditions,^{6,7} however, a somewhat lower barrier should be expected.

Because in a large number of reactions of substituted diazomethanes with phosphacetylene derivatives, the compounds corresponding to **3** and **4** were obtained as the sole products with only a few exceptions,^{6,7} the small energy difference between the two transition structures does not provide a completely convincing basis for a rationalization of the observed product distribution. One of the possible explanations is that the calculations refer to the gas phase, while the experiments are carried out in solution, although the solvents used were not polar. A further possibility is that, in spite of the general expectations, a non-

TABLE III.
Important Structural Parameters for van Der Waals Complexes **3-CO** and **5-CO**.

	3-CO						5-CO					
	a	b	c	d	e	CNN	a	a	c	d	e	CNN
MP2 ^a	1.568	2.958	1.152	1.324	3.302	172.1	1.567	3.266	1.151	1.324	3.205	173.8
MP2 ^b	1.565	2.910	1.144	1.326	3.197	170.6	1.565	3.235	1.143	1.325	3.133	172.7

Bond length are in angstroms and bond angles in degrees.

^{a, b} 6-31 + G* and 6-311 + G* basis sets, respectively. For the notations used see Scheme 2.

concerted pathway toward **3** could be favored over the one via **3-TS**. This will be the subject of further research.

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